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Final Scientific Report

for the 5-Year Period: 1 November, 1984 - 31 October, 1989

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Georgia Institute of Technology

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Entitled

Global Atmospheric Gases Experiment (GAGE)

by

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The GAGE Research Program and its Objectives:

The GAGE program is a team effort involving several institutions in the United States, Great Britain, and Australia to measure and analyze, at five global sites (Mace Head, Ireland; Cape Meares, Oregon; Ragged Point, Barbados; Point Matatula, American Samoa; Cape Grim, Tasmania), a number of long-lived atmospheric trace gases of importance to man and the environment. The site at Mace Head, Ireland was added to the program in 1987. The gases involved are both biogenic and anthropogenic in origin and include the trace species CFCl_3 , CF_2Cl_2 , CH_3CCl_3 , CCl_4 , N_2O , CH_4 , and $\text{CF}_2\text{ClCFCl}_2$. Measurements are made at each site several times daily using automated gas chromatographs. Each of the participating units has its own particular duties and responsibilities and must accomplish its tasks in concert with the other groups. At Georgia Tech, our primary contribution to the GAGE program includes basic processing and calibration of the raw field data from each GAGE station to dimensional form, preparation and presentation of the resulting data base to the GAGE team for discussion and verification, archival and distribution of the final calibrated and verified record, and analysis of the record in preparation for publication of the GAGE results.

The GAGE program is continuing with only the administration of its funding altered. At Georgia Tech, we are now working under a subcontract through MIT (#GC-R-114890) which administers funding for all of the organizations involved in GAGE under a consolidated NASA grant (#GAGW-732). Thus, this "final" report is really only an interim report as far as the total program is concerned.

A Summary of Progress and Results to Date:

Processing of the GAGE raw data from the HP-5880 gas chromatographs

located at each of the five global GAGE sites into final calibrated records has essentially been completed through the period ending in December 1988 and preliminarily through June 1989. Additional F-113 data from Tasmania is being added to that station's data base backward in time as hand analysis of chromatograms can be prepared in Australia and the results shipped to Georgia Tech. While much of this data was collected prior to the onset of the GAGE program, its existence will add substantially to the GAGE record. It is expected that the Tasmanian F-113 GAGE data will extend from early 1982 onward. In general, the lengths of the data records vary from site to site since the GAGE instruments (HP-5880's) were placed into operation as they became available to each station. Except for the Mace Head site, all of the instruments were on line by mid-1985, however.

During the transition period from the predecessor ALE program (which used HP-5840 chromatographs) to GAGE, maintenance of continuity in the overlapping data base was of great concern. To facilitate this process, at least six months of overlap data was recorded and analyzed at each site. At Tasmania, however, more than three years of simultaneous measurements were made and processed. Analyses suitable for comparisons detailing the transition period at each GAGE site have been produced, and the results show clearly that the GAGE data matches the ALE values in considerable detail.

Since the GAGE program is a cooperative effort involving scientists from several organizations around the world, the details of GAGE progress during the program are contained in the "minutes" of the regular semi-annual meetings of GAGE scientists. Copies of the minutes of all such meetings that took place during the lifetime of the current grant are appended as part of this report. In addition, a bibliography of all publications which were produced during the project's 5-year period are attached.

Publications:

Cunnold, D.M., R.G. Prinn, R.A. Rasmussen, P.G. Simmonds, F.N. Alyea, C.A. Cardelino, A.F. Crawford, P.J. Fraser, and R.D. Rosen, Atmospheric Lifetime and Annual Release Estimates for CFCl_3 and CF_2Cl_2 From 5 Years of ALE Data, Journal of Geophysical Research, 91, D10, 10,797-10,817, 1986.

Prinn, R., D. Cunnold, R. Rasmussen, P. Simmonds, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric Trends in Methyl Chloroform During 1978-1985 and the Global-Average OH Concentration, Science, 238, 945-950, 1988.

Simmonds, P.G., D.M. Cunnold, F.N. Alyea, C.A. Cardelino, A.J. Crawford, R.G. Prinn, P.J. Fraser, R.A. Rasmussen, and R.D. Rosen, Carbon Tetrachloride Lifetimes and Emissions Determined From Daily Global Measurements During 1978-1985, Journal of Atmospheric Chemistry, 7, 35-58, 1988.

Prinn, R., R. Rasmussen, P. Simmonds, D. Cunnold, F. Alyea, A. Crawford, P. Fraser, and R. Rosen, Atmospheric Emissions and Trends of Nitrous Oxide Deduced From 10 Years of ALE-GAGE Data, Journal of Geophysical Research, 95, 18,369-18,385, 1990.

APPENDIX

Minutes of the Meetings of the GAGE Scientists

Minutes of the 1st Meeting of GAGE Scientists

Sandy Lane Hotel, Barbados

April 17-19, 1985

I. The meeting began at 8:30 am on Wednesday, April 17 with the following GAGE scientists present: Prinn, Rasmussen, Crawford, Cunnold, Alyea, Fraser, Simmonds and Rosen. Also attending the meeting was W. De More, representing NASA.

The minutes of the 23rd meeting of ALE scientists were approved, and attention moved immediately to the status of the ALE stations. Simmonds reported that the Barbados building was in fine shape, although a new air conditioner will be needed. Simmonds will visit OGC in mid-May to work with the HP 5880 (including CH_4), which will then be shipped to Barbados hopefully in time for installation at the site during June. The group urged that this matter receive highest priority and also recommended that the HP 5840 be allowed to run in parallel with the new instrument at least through December 1985. Rasmussen and Crawford then reported that the floor of the Cape Meares building is sagging and rotting away and will need attention. The HP 5880 there is operating well. The methane addition has not been accomplished yet. At Samoa, a change in NOAA staffing means that a new on-site station manager will be coming. The move into the new building went fairly smoothly, although there were difficulties, such as a failure on the part of NOAA staff to reconnect our air intake lines. The HP 5880 (including CH_4) for Samoa is being tested at OGC, and it is anticipated that it will be on site in July. As for Barbados, the group emphasized that getting this instrument into Samoa is a task of the highest priority. Fraser gave a detailed report on the status of operations at Tasmania. A number of calibration tank supply problems meant that some tanks were on-line for longer than stipulated in the ALE/GAGE

protocol. Also, there were a few power failures in February associated with geese flying into the power lines. Fraser also presented a comparison of monthly mean values from the HP 5880 and HP 5840 at Tasmania and on the basis of these recommended that a 12-month overlap of the two instruments would be desirable. Having well exceeded this period at Tasmania, the group agreed that the HP 5840 should be shut off within the next 60-90 days.

The next item on the agenda was the review of ALE data. Rasmussen noted that although certain issues concerning N_2O in primary standard tank 033 remain unresolved, he is now certain that there is no "drift" problem affecting the first five years of ALE data, and these data can now be considered final. Rasmussen also reported that a first draft of the ALE VII paper on N_2O will be distributed in mid-June. The group agreed to delay release of the 5-year data tape until that time. Data for the first half of year 6 (July-Dec. 83) were briefly reconsidered and approved, and then the 9 action items for the second half of year 6 (listed in the minutes of the 23rd ALE scientists meeting) were each considered in turn. All of these items have now been dealt with except for item 8 involving the use of an "internal standards method" to deal with a carrier gas problem at Tasmania. The first look at year 7 (July-Dec. 84) HP 5840 data produced the following set of new action items:

Barbados

1. Pollution events in November to be rechecked, along with the drop in most species prior to the major pollution event that month
2. Values during Sept. 1-5, during a possible "interhemispheric exchange" event, to be rechecked
3. "In" value for tank 249 to be incorporated

Oregon

4. HP 5840 data (available only through July 84) to be compared with HP 5880 data

Samoa

5. Data in early November during week after move into new building to be reconsidered

Tasmania

6. CCl_4 and CH_3CCl_3 values during reign of tank 248 to be reconsidered
7. Values of CCl_4 and CH_3CCl_3 during the "burp" from Aug. 27-mid Sept. to be reconsidered
8. "In" value only to be used for tank 248 for N_2O ; similarly, "in" value only to be used for tank 268 for N_2O

The first session then adjourned at 1 pm.

II. The meeting resumed at 2 pm with Fraser displaying time series of HP 5880 data for 1984 at Tasmania. This led to two additional action items: (a) the HP 5880 data need to be placed into "ALE" format; and (b) the "in" value for tank 288, associated with a big jump in N_2O , CCl_4 and CH_3CCl_3 , needs to be determined.

The issue of automatically processing the HP 5880 data to produce ALE-type time series in the future was addressed next by Alyea. He suggested formats for transmitting the data to Georgia Tech., which the group tentatively agreed upon. Some of the software difficulties involved in interfacing the HP 5880 with the Techtran recording unit were discussed at great length, but it became clear that these problems were not insoluble. Cunbold suggested that some means ought to be found to automate the identification of pollution events at a station, and the group agreed that this subject should be discussed again at the next GAGE meeting.

Prinn discussed the issue of occasional "quantization" of ALE data which occurred when the precision of the measurements was less than ideal, such as when it was necessary to resort to peak heights. The group agreed that this problem does not affect the major goals of ALE/GAGE, and moreover the problem should not exist with the high precision HP 5880 data, in which four significant figures will be retained.

The rest of this session dealt with administrative matters. Most of the investigators reported that they had their grants/contracts in hand. Rosen noted, however, that AER had not yet received its contract in writing, although verbal assurances have been given by NASA procurement personnel that it was on its way. In light of the delay in getting funding to the GAGE investigators, De More suggested that budgets for the second year of GAGE be submitted as soon as possible. Simmonds reported on NOAA's expression of interest in contributing to the support of the Barbados station, and he will follow up on this. Prinn pointed out that the scientific community has been urging that the Adrigole station be reinstated, and the group agreed to continue to pursue means for doing so. Prinn also remarked that interest is building in establishing a real-time GAGE station in the Aleutians (possibly at Shemya), downwind of the Soviet fluorocarbon source region.

Venues for future GAGE meetings were discussed next. It was agreed that the next meeting be held at MIT's Endicott House in Dedham, Mass. in October. It was also agreed that people from NOAA GMCC should be invited to meet with the GAGE team for one day at this time to compare data and discuss future cooperation. Prinn will finalize the dates and other arrangements for this meeting as soon as possible. The third meeting of GAGE scientists in April 1986 will be arranged by Rasmussen for a location on the west coast.

Prinn briefly reported on the outcome of a recent workshop on global tropospheric chemistry held in Boulder and attended by over 100 scientists. Program managers from NASA, NOAA and NSF were also present at the workshop and expressed much interest in coordinating a major research effort on the subject. Several of the goals for trends and distributions relevant to tropospheric chemistry agreed upon at the Boulder workshop are being, or will be, met by the GAGE data set; moreover, the Boulder group endorsed the reopening of the Adrigole station and the establishment at Shemya of a GAGE-type station.

The session then adjourned at 5:45 pm.

III. The meeting resumed the next morning at 8:30 am with Cunnold leading a lengthy discussion of ALE VIII on the five-year data set. To keep the paper a manageable size, Cunnold has presented results for F-11 and F-12 only. (The other species will be reported on in a separate paper.) The GAGE scientists agreed to review the paper and to give comments directly to Cunnold.

Plans for a paper (ALE IX) on seasonal and higher frequency fluctuations in the species data due to meteorological forcing do exist, but Rosen reported that budget constraints will delay preparation of a first draft for another year. Fraser indicated that ALE X, dealing with comparisons of HP 5840 and HP 5880 time series, is being worked on.

For the next several hours the discussion focused on the desirability of adding carbon monoxide to the suite of chemicals being measured at the GAGE stations. Prinn noted the importance of determining the global trend of CO, because of its role in regulating tropospheric OH concentrations. In this regard, Rasmussen remarked that the 6% per year trend in CO reported in his Tellus paper using 3 years of data no longer existed, and, in fact, based on 5 years of CO

measurements, there is no discernable trend in this species. The usefulness of measuring CO at a few isolated surface stations, given its large degree of spatial heterogeneity, was discussed at length in light of future plans to monitor CO from satellite. It was agreed that GAGE measurements of CO would serve as important "ground truth" for such satellite measurements, and also that GAGE data on CO in conjunction with measurements of the other GAGE species, could help discriminate natural sources of CO from anthropogenic sources. This latter point requires further consideration, and given its potential importance, the group agreed to do so.

The session adjourned at 1 pm.

IV. The final session of the formal meeting began at 2 pm. Alyea reported that the proposal by Atlanta University Center to establish a GAGE-type station was not received with interest by NASA. Alyea also reported on information he received that China is manufacturing fluorocarbons in six cities and that the Chinese would be willing to produce an inventory of their production if a small amount of funding could be made available for this purpose. Alyea will pursue the matter further.

Rasmussen and Prinn spoke of their interaction with Russian scientists, who seemed genuinely interested in cooperating with the GAGE team. Follow-up on this matter depends next on a Russian response to our offer of an HP 5840 in return for their providing us with the results of their measurements on this machine.

The first meeting of GAGE scientists formally adjourned at 3:00 pm so that the group could travel to Ragged Point to visit the GAGE station. Informal meetings among several of the GAGE scientists to discuss outstanding issues including an Adrigole proposal were held on Friday, April 19.

MINUTES OF THE SECOND MEETING OF GAGE SCIENTISTS

MIT Endicott House, Dedham, MA
October 23-24, 1985

I. The meeting began at 9:00 am on Wednesday, October 23 with the following GAGE scientists present: Alyea, Crawford, Cunnold, Khalil, Fraser, Prinn, Simmonds, Rosen.

The minutes of the first meeting of GAGE scientists were approved, and attention turned to the status of the GAGE stations. Simmonds reported that NOAA has written a two-year contract to help support the Barbados station; the remaining half of the needed funds will be supplied by the CMA. At the site, a new air conditioner has been installed, and the building is in fine shape. The HP 5840 is now running beautifully, although it was down for 3 weeks during late June to mid-July because of problems following a burned-out pump relay. The HP 5880 finally arrived in Barbados on August 3 after a number of shipping delays. Several problems were encountered in setting up the 5880, including difficulties with the compressor and the program, but it seems to be running well as of mid-October. For several of the species, the data from the 5880 are not looking as good as those from the 5840, but this situation should improve as the 5880 start-up problems are worked out. A real difficulty, though, is with the new CH_4 measurements which are currently much noisier (few percent precision) and at a higher level (up to 2 ppm) than expected. This led to a lengthy discussion about possible sources of contamination and possible remedies. This is a general problem since it was noted by Crawford that the CH_4 measurements at Samoa and Cape Meares are also suffering from high noise levels (it was discovered subsequent to the meeting that cross-contamination involving the valves was the cause of the problem at all sites and this has now been fixed).

Crawford reported that the Oregon Dept. of Parks has complained about the appearance of the building at Cape Meares, so it will have to be replaced. The HP 5880 has been running since mid-July and, except for the CH_4 problem, is producing good quality data. The 5880 in Samoa was also installed in mid-July, but a shortage of carrier gas led to a loss of 2 weeks of data on the 5880, a month on the 5840. This will necessitate postponing the planned shut-off date for the 5840 until early 1986 to permit the desired 6-month overlap period. The need for an overlap period is straining budgets at both Samoa and Barbados, however, and it was agreed to allow the field scientists to decide about closing down the 5840 prior to the next GAGE meeting, subject to the constraint of having at least 6 months of overlap data and in consultation with other members of the GAGE team. A completely new NOAA team is now on-site at Samoa, and (conversant with Reagonomics) a meter has been installed to monitor, and charge for, our electricity usage in the new building.

At Tasmania, plans call for the CH_4 detector to be added to the 5880 during Crawford's visit in early December. The 5840 was shut off on July 2; shortly thereafter, the 5880 developed its first instance of a serious malfunction in its 4-year lifetime (Murphy's Law?). The machine was down for about 2 weeks but is now back in operation. The most recent calibration tanks were on-line for 8 months, but it is hoped that shorter tank usage times will be possible in the future.

The first session adjourned at 12:30 pm.

II. The meeting resumed at 1:30 pm with Alyea reviewing the difficulty with the CCl_4 and CH_3CCl_3 5840 data at Tasmania for April - October 1984. Although he and Crawford attempted a number of remedies, none were especially satisfactory, and it was agreed to delete these data from the record.

Next, attention turned to reviewing data from the first half of year 7, July 84 - December 84, in light of the 8 action items from the previous GAGE meeting. Six of these have been attended to, but the Oregon 5880 data for July 84 have not been transmitted to Alyea yet for comparison with the 5840 data that month. In addition, it was decided to reverse the action item regarding the treatment of calibration tank values for N_2O at Tasmania (see below).

Data for the second half of year 7, January - June 85, were inspected for the first time, leading to the following set of new action items:

- Barbados:
(5840)
 - 1. Check CH_3CCl_3 data during several-day period during mid-February when high values occur,
 - 2. Check data in early May associated with jump in CH_3CCl_3 , F-11 and F-12,
- Samoa:
(5840)
 - 3. check data on S-column and F-11P during January "burp",
- Tasmania:
(5840/5880)
 - 4. Review the entire HP 5840 data for this period - it was unavailable at GAGE 2 meeting,
 - 5. Regarding the HP 5880 data, check all species during January 11-15,
 - 6. Return to the first half of year 7 and reverse the previous decision to use only "in" values on tanks 248 and 268 for N_2O ; instead return to normal procedure of averaging "in" and "out",
- Oregon:
(5880)
 - 7. Fill in data missed because of intermittent loss of Techtran recording,
 - 8. check CCl_4 (and F-113) during January when large amplitude oscillations occur.

During the inspection of the most recent data at Samoa, it was noted that the noise level has increased on all species since the move to the new building.

The issue of how many 5880 measurements should be reported "by hand" when the automatic recording system fails was discussed next. It was agreed to limit these data to 4 times daily (0300, 0900, 1500, 2100 local time); when the Techtran link is operating, the 12 times daily frequency will be maintained, of course. In this connection, it was agreed that the "CACA" sequence of measurements will be the GAGE standard. Fraser will assess the difficulty of implementing this operation at Tasmania.

Alyea reported his plans for analyzing the pre-GAGE 5880 data from Cape Grim. He expects to work back 6 months at a time and hopes to complete processing all the data back to 1981.

The first day's session closed with a discussion of funding matters. Rosen announced that a contract had finally been signed between AER and NASA, effective from September 1985 through March 1988. Other team members supported by NASA have already submitted their renewal proposals for their second year of funding. Simmonds noted that the U.K.'s Department of the Environment (DOE) has expressed interest in reopening the Adrigole station. He will stay in touch with Prinn on this development to coordinate a proposal to NASA to supply a new instrument for this site.

The session adjourned at 5:00 pm

III. The meeting resumed at 9:00 am on Thursday morning with Rasmussen joining the group. The morning discussion centered on reviewing the agenda for the joint meeting to be held the next day (Friday, October 25) with GMCC scientists (A transcript of this GMCC/GAGE meeting was made and distributed to all participants. A second meeting was planned once GMCC had one year of finalized HP 5890 data at Samoa). This wide-ranging discussion included such matters as the independence of the two programs and the desirability of setting up a new GAGE site at Shemya.

Venues for future GAGE meetings were discussed next. It was agreed to hold the next GAGE meeting in the Pacific Northwest during the week of April 28 - May 2, 1986. Rasmussen will handle the arrangements. Tentative plans were made to hold the 4th meeting of GAGE scientists in Australia at the end of November. Fraser will investigate the feasibility of hosting the meeting in Australia; if this is not possible, the meeting will be held in the Atlanta area.

Rosen asked for the group's consent to destroy old data sheets and punch cards containing ALE data more than 3 years old. Because adequate backup for these data exist elsewhere, the group agreed that the AER "paper" records could be destroyed.

IV. After a brief lunch break, the final session of the meeting turned to the status of planned ALE papers. Khalil indicated that ALE VII, on nitrous oxide, should be ready in a few months. One snag in this work has been the sensitivity of trend estimates for N_2O to data jumps associated with calibration tank changes. Cunnold reported that the 5-year F-11, F-12 paper was submitted to JGR in mid-September. He asked for comments from other GAGE team members. Cunnold noted that the next paper on CH_3CCl_3 and CCl_4 is about 1/3 completed. A lengthy discussion was held regarding the input needed to finish this work.

The second meeting of GAGE scientists ended at 3:00 pm.

MINUTES

The Third Meeting of GAGE Scientists

Kah-Nee-Ta Resort, Warm Springs, Oregon
April 29-30, 1986

(I)

The meeting began at 9:00 am on Tuesday, April 29, with the following GAGE scientists present: Prinn, Crawford, Khalil, Rasmussen, Cunnold, Alyea, Fraser, Rosen, Simmonds.

After quickly approving the minutes of the second meeting of GAGE scientists, the group turned its attention to the data that had been collected by the HP 5840 and 5880 instruments at the various sites. The following items were agreed to for each station:

Tasmania (5880)

1. It was agreed to begin the data record with the start of tank 168 in December 1981.
2. Item 5 of GAGE 2 minutes still to be done (Check all species during January 11-15, 1985).
3. Check the chromatograms around the time of major step jumps associated with tank changes, as in transition from tank 130 to tank 288 in December 1984. Tank 130 calibration values to be rechecked.

(5840)

4. Data from P-column to be checked and deleted, if necessary, during January 1985 because of instrument problems.

Samoa (5840)

5. Check jump in data in early December 1985 related to carrier gas change.
6. Trajectory analysis to be performed in connection with January 1985 "burp".

Barbados (5880)

7. Delete F-113, CH_3CCl_3 and CCl_4 data during August-October 1985 because of regulator problems.
8. Check CH_3CCl_3 during first 10 days of November 1985, which is much noisier than 5840 measurements.

Oregon (5880)

9. Check tank 290 values for CCl_4 in September 1985.

10. Check species values in late January 1984 after system restart.
11. Check jump in F-11 associated with transition from tank 286 to tank 283 in May 1985.

It was also noted that the precision of methane field analyses was significantly less at Barbados and Oregon than typically obtained with HP 5880's equipped with FID's in laboratory conditions.

The first session then adjourned at 12:00 noon.

(II)

The second session resumed at 2:00 pm with a discussion of how to merge the overlapping HP 5840 and 5880 data to produce a "GAGE recommended" overall data set. It was agreed to derive a "GAGE recommended" daily mean value by optimally combining the 5840 and 5880 data during a 6-month period (chosen when both instruments are operating best), taking into account the standard deviations of the measurements from each instrument. Other techniques, such as simple averaging, will also be tested, and the results will be presented at the next GAGE meeting.

The rest of the afternoon session dealt with reports on the present status of the GAGE stations. Simmonds reported that the air conditioners at the Barbados site were becoming very short-lived, and that the pump for the air compressor was also unreliable. The HP 5840 at Barbados is to be shut off on April 30. Simmonds also noted that there has been a real problem with the logistics for receiving calibration tanks, to the extent that he has run out of gas. Rasmussen explained that a source of the difficulty has been the lack of newly manufactured cylinders that pass GAGE standards, and that recycled tanks have begun to leak. A new manufacturer has been located, however, and Rasmussen expects the short supply of tanks to be alleviated by summer.

Crawford reported that the Cape Meares building is still intact, although the ground's slope is noticeably increasing. A purchase order for a new building that will pass the approval of the Oregon Dept. of Parks has been placed, and OGC will seek a funding supplement from NASA for the costs involved. Methane measurements at Cape Meares are still not sufficiently precise, and Rasmussen noted that the lack of an HP 5880 in the laboratory has posed real difficulties in tracking down problems in the field. The group endorsed Rasmussen's suggestion that he seek funds for another instrument. The group also asked that the HP 5880 in Tasmania be immediately set up for methane measurements as required by the GAGE plans (additional insight for improving methane precision may also come from this).

The HP 5840 at Samoa will be shut off during Crawford's visit in June. The new NOAA operation at Samoa has not yet begun. Fraser concluded the session with a thorough report on the status of the Tasmania station. Highlights since the last GAGE meeting include an air conditioner leak during January and a lightning strike in November that rendered instruments inoperable. Apparently the Tasmanian Devil problem is licked.

The second session adjourned at 4:30 pm.

(III)

The meeting resumed at 9:00 am on Wednesday morning with Khalil presenting some preliminary results on N_2O trends. Among the key points he made were that the trend was quite variable in time and that there was a close correspondence between flask and gas chromatograph measurements at the same site. Khalil indicated that a paper on the N_2O results will be prepared this calendar year. Finally on the subject of N_2O , the group formally adopted a calibration factor of 0.91 to be applied to the GAGE measurements.

Cunnold reported that the 5-year paper on F-11 and F-12 results has been revised in response to reviewer comments and returned to JGR. Drafts of papers reporting on CH_3CCl_3 and CCl_4 based on 6 years of ALE/GAGE data are now in preparation. Based on a new release scenario and a new calibration factor, both the trend and the inventory approaches yield similar lifetime estimates for CH_3CCl_3 of about 6 years. Moreover, results from all stations for this species are now consistent. As for CCl_4 , there is a large disagreement between the trend and the inventory lifetime estimates, regardless of the release scenario. There is also a large sensitivity in both approaches to the release scenario. It is clear that the current uncertainties in absolute calibration and in releases are too large to permit any reasonable conclusions to be made about the lifetime of CCl_4 . Instead, Prinn suggested that calculated "photodissociation-only" lifetime estimates be used, in combination with the GAGE data, to provide estimates of the release of CCl_4 .

Fraser reported that a paper comparing HP 5880 and HP 5840 measurements at Cape Meares and at Tasmania is now in a formative stage. The group agreed that such a paper would be the best place to discuss techniques for blending the two data sets, if this material could be included in a timely fashion.

The meeting focussed next on a number of issues related to funding. Simmonds noted that CMA support for the Barbados station has been secured, but that the NOAA share has yet to be completely committed. Simmonds will follow up with NOAA on this matter in the near future. Simmonds and Prinn also informed the group of efforts to reopen an Ireland station at Macehead, some 1.5° north of the Adrigole site. Based on the greater likelihood of long-term, sustained funding at Macehead than at Adrigole, the group endorsed the proposal that Macehead serve as a GAGE station. Simmonds and Prinn hope to open this new site by the end of 1986. In addition, the Adrigole station will be reactivated to permit a 6-month overlap period with the Macehead station. As for a N.W. Pacific GAGE station, the group was informed by Joe Prospero (via Prinn) of serious drawbacks to the Shemya location, and no further resolution on this subject was achieved at the meeting.

The next meeting of GAGE scientists was set for November 21-23, 1986, in the Melbourne, Australia region. Paul Fraser will serve as host, and he will notify team members of the final arrangements as soon as possible. Tentative plans for a March/April 1987 meeting in Georgia were also agreed to; Alyea and Cunnold will present further details at the next GAGE meeting.

The third meeting of GAGE scientists ended at 1:00 pm.

Minutes of the Fourth Meeting of *GAGE* Scientists
Peninsula Country Golf Club, Frankston, Victoria, Australia
November 20-23, 1986

I. On Thursday, November 20 the *GAGE* scientists visited the *CSIRO* Division of Atmospheric Research. The *GAGE* meeting began formally on Friday with the following *GAGE* scientists in attendance: Prinn, Rasmussen, Cunnold, Alyea, Simmonds, Khalil, Crawford, Fraser. Rosen could not join the meeting until the afternoon of Friday, November 21, and the record prior to his arrival was taken by Prinn and Fraser.

The reports on the present status of stations began with Ragged Point, Barbados. Simmonds reported that there have been continual problems with the clean air generators, three having failed in the first year. A German compressor will be tried next. In addition, the UPS blew up because of a power outage, and although it has been repaired, its current status is uncertain. Air conditioner problems also continue to exist at the site. The source of ripple noise on the porasil channel was finally traced to a piece of septum flapping in the carrier gas stream and was fixed. Simmonds pointed out that he has no backup boards for the HP 5880 nor any backup detectors. In combination with the problems noted above, he therefore will need to request additional funds from NOAA/CMA in his next budget submission. Finally, Simmonds noted that a serious problem exists with calibration tanks running out.

Crawford and Rasmussen next reported on the status of the Cape Meares, Oregon station. The new building has been ordered and should arrive by the end of this year. It will be 2 feet longer than the present building. the installation will take about 1-2 weeks, during which time flask samples will be taken. Many more people appear to be visiting the area, now that the lighthouse has been opened nearby. The HP 5880 is working well. Episodes of erratic CH_3CCl_3 behaviour have started up again, perhaps because of meteorological conditions. Difficulty still exists in obtaining the precision wanted for the CH_4 measurements.

At Samoa, the HP 5880 is working well, according to Crawford and Rasmussen, although there is a rotor problem on the porasil channel. Since June 1986, the 5880 has been interfaced with an IBM, which is proving to be much better than the Techtron.

Fraser provided an extensive report on the status of the Cape Grim station. Highlights include the installation of the *GAGE* methane instrumentation, and the development of software to process both the CH_4 and $F-113$ data. A problem has developed with N_2O measurement noise since the methane instrumentation was installed. Moreover, a serious budgetary problem has arisen in connection with the introduction of the *GAGE* methane program, because of the considerable costs involved for additional gases. Rasmussen volunteered to repair an OGC zero air generator for use at Cape Grim to alleviate this problem.

Finally, Prinn and Simmonds reported on the progress of plans for the new *GAGE* station at MaceHead, Ireland. Funds have been provided to MIT from NASA to purchase the instrument, and the UK DOE has agreed to support the costs of operating the station for at least one year. Present plans call for the new station to begin operating early in 1987.

Discussion turned next to the options available for improving the precision of methane measurements at the *GAGE* stations. The performance of the HP 5880's has been somewhat disappointing thus far, most likely because of back diffusion of CH_4 from the carrier gas used for the *ECD*'s. (Evidence for this suggestion was provided by the notable improvement in the CH_4 measurements at Samoa when the carrier gas ran out.) The station scientists agreed to use the (more-accessible) instruments in Ireland, Oregon, and possibly Tasmania to solve the difficulty with the methane measurements.

II. The review of data taken by the HP 5840 and 5880 instruments at each station occupied much of the meeting on Friday and Saturday. HP 5840 data was examined for the period from January 1985 through the end of their record at each station. The following action items regarding these HP 5840 data were agreed to:

(A) 5840 data (Jan 85 to shut-offs in 86)

Barbados

- (a) CH_3CCl_3 Dec 15-25, 1985, high values to be checked
- (b) tank 246 "in" value to be included for 1986 data
- (c) increases in $F11S$, $F11P$, $F12$, and CH_3CCl_3 just prior to tank 307 to tank 246 change in 1986 to be checked

Samoa

- (d) Jan 7 - Feb 15, 1986, jumps in all halocarbons to be checked
- (e) last 4 days of operation (April, 1986) to be checked for noise problems for all species

Tasmania

- (f) Jan 4-31, 1985, N_2O data to be tossed out due to temperature regulation problems

The HP 5880 data were examined from the beginning of their records at each station, and the following actions were agreed to:

(B) 5880 data

Tasmania

- (a) April 12, 1982, CH_3CCl_3 "key 7" data anomalously high and should be checked
- (b) March 10, 1982, CCl_4 , CH_3CCl_3 , $F11P$ all below baseline after data gap - check
- (c) September 20-25, 1982, $F12$ high values to be checked
- (d) July 2, 1984, 12:15 pm ambient measurement of CH_3CCl_3 to be checked
- (e) December 1984 check noise on $F11S$
- (f) January 4, 1985, 11:18 am and 4:16 pm check CH_3CCl_3 data
- (g) August-December 1985, quantization problem evident - check for integration anomalies
- (h) hand integrate data for a 1-week period in April 4 - June 30, 1986, then hand integrate 4 per day over entire period if automatic integration problem was evident
- (i) tank 324 returned very low - include values for everything but CCl_4
- (j) for $F - 113$ at all stations, make vertical scale extent about 20 pptv (c.f. 50 pptv at present)

Samoa

- (k) early December 1985, reasons for gap followed by jump in all species
- (l) S column jumps associated with tank 322 to 025 change in June 1986 to be checked
- (m) check methane record vs. P-column status to give clues about methane precision

Barbados

- (n) delete $F - 113$, CH_3CCl_3 and CCl_4 data in late October 1985 due to regulator problems
- (o) investigate further the difference between early November 1985 HP 5880 and HP 5840 CH_3CCl_3 data
- (p) check "key 7", April 1986, N_2O

Cape Meares

- (q) March 1984, dip in methyl chloroform (and some other species) to be investigated
- (r) May 1984, $F - 113$ step jump involved with change from tank 261 to 265
- (s) January 1985, CCl_4 erratic behavior to be studied in connection with CH_3CCl_3 pollution
- (t) September 1985, CCl_4 to be dropped because tank 290 values are drifting
- (u) December 1985, CCl_4 and all other species to be eliminated on "*shoulders of suspected pseudo-pollution*" (WOW!) event
- (v) March 1986, $F - 113$ jump to be investigated (may be a transcription problem)

III. After completing the data review during the session on Saturday, November 22, attention turned to the remainder of the agenda. Alyea reported that, because of the large effort involved in processing all the HP 5880 data that became available during the last six months, little attention was paid to techniques for merging these data with those from the HP 5840. A lengthy discussion ensued about the best approaches to this task and about the needs of other potential users of the *ALE/GAGE* data set. It was agreed that Alyea would produce plots of the overlapping data records for all species and all stations at the next *GAGE* meeting; it was also agreed that Fraser and Rasmussen would prepare a draft of a manuscript discussing the overlapping data records in time for this next meeting.

The site of the next *GAGE* meeting was chosen to be Calloway Gardens in Pine Mountain, Georgia for April 14-16, 1987. Cunnold and Alyea will serve as hosts. Plans for the fall 1987 *GAGE* meeting were not set, although some sentiment was expressed for a west coast US locale.

A number of papers being prepared for formal publication were discussed next. A draft of a manuscript about CH_3CCl_3 was circulated by Prinn and all co-authors agreed to provide written comments to Prinn as soon as possible. Similar action was agreed to regarding the manuscript about CCl_4 prepared by Cunnold (discussion of this manuscript focused on what is currently known about the absolute calibration of CCl_4). Khalil reported that some progress has been made on the N_2O paper, with important insights having been gained by waiting for the data record for this species to grow long enough.

Rasmussen reported that a "retired" *ALE* HP 5840 will be shipped to the Soviet Union as soon as formal arrangements can be completed. The Russian scientists agreed in return to send the data taken by this instrument back to Rasmussen. The group received the news of this development with much interest and enthusiasm.

Finally, the group agreed that it was premature to discuss the addition of CO measurements to the *GAGE* program at this stage, given the uncertainties still surrounding the CH_4 measurements. However, CO remains of keen interest and will be discussed more fully at the next *GAGE* meeting.

The fourth meeting of *GAGE* scientists adjourned at 1:30 pm on November 22. Subgroup meetings were held on November 23 as required.

Minutes of the Fifth Meeting of GAGE Scientists
Callaway Gardens, Pine Mountain, Georgia
April 14-16, 1987

I. The meeting began on Tuesday, April 14 at 9:30 am with the following GAGE scientists in attendance: Prinn, Alyea, Cunnold, Cardelino, Rasmussen, Crawford, Fraser, Rosen, and Simmonds.

The minutes of the previous meeting were quickly approved, and attention turned to reports on the present status of the stations. Simmonds reported that there has been a problem with the silicone channel at the Barbados station, causing intermittent losses of CH_3CCl_3 and CCl_4 especially in January and February 1987. Although the UPS at Barbados had been repaired, it still may not be working properly, although this matter is still being evaluated.

Simmonds reported the good news that the new GAGE station at Mace Head, Ireland began operations on January 23. Although the wintertime is a period of frequent pollution events in Ireland, the data being taken appear to be quite reliable. A competent caretaker for the station (Duncan Brown) has been hired. Problems with the power supply at Mace Head may be a continuing worry; power was shut down for 12 days in February to rewire the peninsula. Plans were made to overlap the Mace Head data with new measurements to be made at Adrigole during May-July, although Simmonds was concerned about how well the HP5840 at Adrigole will function after having been shut down for two years. Rasmussen promised to supply a calibration tank to Adrigole within the next month. On the subject of calibration tanks, Rasmussen reported that the difficulties in producing new tanks appear to have been resolved and that new tanks should be available in about 3-6 months. In the meantime, the old tanks are being recycled, although they are not standing up well to this process.

Crawford reported that the new building at Cape Meares, Oregon was installed at the end of January. The installation was completed within 8 days. The only problem has been with the new air conditioner, which is being replaced this week. The measurements in the new building have been excellent, except for diurnal noise in the data due to the air conditioner problem. In particular, the methane data look especially good now. As part of the new facility, weather data are being obtained at the site.

Crawford made a site visit to Samoa in January and discovered that the UPS was not operating. As a result, the HP5880 had been going on and off several times per day, causing a host of problems. The UPS was shipped to the manufacturer for repair, and Crawford re-installed it in mid-March. The problems with the UPS at a number of stations led to a general resolve to investigate ways to improve this situation. Similar concerns about the zero-air generator were also expressed. Rasmussen expressed dissatisfaction with the continuing lack of cooperation from NOAA at Samoa, and the group agreed that this was a problem. Finally, Crawford noted that, as in Barbados, the carrier gas at Samoa had saturated the mole sieve, and the nafion drier was also saturated. These problems were corrected during his maintenance visit.

Fraser presented a detailed written report about the status of the Tasmanian station. One item that engendered a lengthy discussion was the problem being experienced in obtaining N_2O measurements, which have become quite noisy during the last year. A number of possible sources for the difficulty were discussed, with the most likely explanation being contaminated carrier gases. Among possible solutions suggested was the use of coconut charcoal in the mole sieve, but it was generally agreed that first priority ought to be given to securing purer carrier gases.

On general experimental topics, the group viewed with satisfaction the overall improvement in the precision of the methane measurements being made at the GAGE stations. Fraser expressed concern, however, about the constraint currently imposed by having only three significant figures from the HP5880s for the CH_4 integration. Although this still implies a precision that is sufficient for the GAGE goals, it will eventually be desirable to have additional resolution. This matter will be investigated further. The difficulty in continuing to obtain Porasil D was also discussed, and despite problems with tracking down the source for this material, efforts will still be made to do so.

The first session of the meeting adjourned at 1:00 p.m.

II. The meeting resumed at 2:30 p.m. with a review of data action items left from the last meeting. Listed below are those action items that still require attention (letters in parentheses refer to the list from the minutes of the Fourth Meeting of GAGE Scientists):

(A) 5840 data

Barbados

- (a) Tank 246 to be rechecked for CCl_4 , since in and out values differ greatly (item b)

Tasmania

- (b) Ensure that January 1985 N_2O data have been deleted (item f)

(B) 5880 data

Tasmania

- (a) Record of comments regarding high values of F12 during Sept. 20-25, 1982 to be checked to look for further explanation of this behavior (item c)
- (b) Noise on F-11S during December 1984 to be pursued by making sure that all VV integrations have indeed been removed and by removing all VP integrations (item e)
- (c) January 4, 1985, 11:18 a.m. and 4:16 p.m. CH_3CCl_3 data to be checked again (item f)
- (d) April-June 1986: Check few low N_2O values that resulted from hand integration; also recheck key 7 F12 values during this period (item h)
- (e) Tank 324 in values to be included for everything except CCl_4 (although tank was returned empty, Crawford cryotrapped the emptiness and obtained reasonable values except for CCl_4) (item i)

Samoa

- (f) Clues about methane precision to be sought further when new data are returned (item m)

Barbados

- (g) All CH_3CCl_3 data prior to early November 1985 tank change to be eliminated and values after tank change to be reinstated (item o)

- (h) Late April 1986 N_2O values to be dropped because of integration problems (item p)

The following action items deal with new GAGE (HP5880) data for the period July-December 1986:

Samoa

- (a) Drop F-113 during mid-June to mid-July
- (b) Variability during December to be investigated further by checking key 7, etc. in order to determine possibility of local pollution vs. cross-hemisphere flow.

Tasmania

- (c) N_2O to be redone by hand
- (d) For all species, remove data during periods in October when cal tanks were shut off
- (e) Check F-113 during October-December and either discard or replace

Oregon

- (f) Somewhat noisier behavior of F-11S in December to be checked

Barbados

- (g) Check all species during Dec. 5-30 when water problem existed
- (h) Check F-11P during August-October when it appears noisy

The first day of the meeting adjourned at 6:30 p.m. ,

III. The second day of the meeting began at 9:15 a.m., Wednesday morning. Alyea presented initial results of comparing HP5880 and HP5840 data during the periods of overlap at the various stations. A number of suggestions were offered for further quantitative comparisons, which will be needed for a paper being prepared by Fraser on this subject

Attention next turned to the status of papers being prepared for formal publication. Rasmussen indicated that the data analysis has been completed for the N_2O paper and that a draft of the manuscript is being prepared by Khalil. Prinn circulated a new draft of the CH_3CCl_3 paper and asked that

comments be given him quickly, since he plans to submit the paper to Science shortly. Cunnold also circulated a new version of the CCl_4 paper, and a lengthy discussion ensued regarding the best approach to deal with the nonlinearity in the CCl_4 production trend. Finally with regard to papers, it was agreed that Fraser will take the lead in producing a F113 paper that will combine the longer record at Tasmania with the shorter records at the other stations. The subject of absolute calibration values for F113 will be placed on the agenda for the next GAGE meeting.

The next meeting of GAGE scientists will take place at a Pacific Northwest locale during November 9-20 to allow the team to visit the new Cape Meares station. Rasmussen will serve as the local host and finalize arrangements. It was agreed to hold the following meeting in May 1988 in the vicinity of the new Mace Head, Ireland station. Simmonds will report details at the next meeting.

Prinn noted that Dixon Butler of NASA had indicated that renewed funding for GAGE need not require peer review, and Prinn suggested that Rasmussen inquire whether this also included the experimental components of GAGE as well. Simmonds received encouraging news from NOAA and CMA regarding continued funding for Mace Head for the next 1-2 years. The impact of the newly organized EROS project on the future of GAGE was discussed next. Although originally intended to deal with aerosols and short-lived trace species, EROS seems to have expanded to incorporate some of the goals of GAGE. The group felt it would be useful to obtain further information about EROS and will discuss this at our next meeting.

The addition of CO measurements to GAGE was briefly discussed. Rasmussen indicated that he had received some support from NSF to investigate the feasibility of measuring CO (among other species) and was now preparing a larger proposal to NSF to implement such measurements at three Pacific locations. It seems reasonable, therefore, to consider a GAGE proposal to NSF to include the GAGE Atlantic sites and Tasmania in such a program. This subject will be explored more fully at the next GAGE meeting.

The fifth meeting of GAGE scientists formally adjourned at 1:15 p.m. Informal subgroup meetings were held during the remainder of the afternoon and into the next day.

AGENDA

Minutes of the Sixth Meeting of GAGE Scientists

Salishan Lodge, Oregon
November 17-19, 1987

I. The meeting began on Tuesday, November 17 at 9:15 am with the following GAGE scientists in attendance: Prinn, Alyea, Cunnold, Simmonds, Fraser, Crawford and Rosen.

The minutes of the previous meeting were accepted without change, and attention turned to reports on the present status of the stations. Simmonds reported that the last several months have been a disaster at the Ragged Point, Barbados station, necessitating an emergency visit there in August. Among the litany of problems: the zero-air generator blew up, the on-line calibration tank ran out because of caretaker error, the UPS has proven to be worthless, and flame photometric detector problems have yielded less than optimal CH_4 measurements. Most of these problems have now been resolved, although it took all of Simmond's remaining budget to do so. A new caretaker (Peter Sealy) has been hired. Although these problems resulted in a loss of ~ 1 month of CH_3CCl_3 and CCl_4 data, most of the fluorocarbon data was not affected. Difficulties with the CH_4 measurements still remain, however. Simmonds also reported that the AEROCE program was starting a major construction project at Ragged Point.

In contrast to the problems at Barbados, the Macehead, Ireland station has been behaving wonderfully. Simmonds reported that good data have been obtained since March 1. A good caretaker has been found, and relations with the nearby University College are excellent. AEROCE is also building a station at Macehead, upwind of us. Elsewhere in Ireland, Simmonds managed to restart the old Adrigole HP 5840, but only after considerably overhauling the instrument. The silicone channel is not functioning, but he hopes to acquire at least three months of data on the Porasil channel to overlap with the Macehead measurements. A preliminary comparison of data from the two sites is very encouraging, showing that they are both sampling the same air masses.

Crawford reported that the Cape Meares, Oregon station had experienced a number of problems, because of a lack of temperature stability inside the building. A newly installed indoor temperature sensing system seems to have solved this difficulty. Methane measurements continue to be noisier than desired, however. Weather instruments have been added to the station, and information from these will be included with the species data. Finally, a break-in did occur at the building, but damage was slight.

Crawford visited Samoa earlier this month and everything is currently in good working order, including the zero-air generator and the UPS. In this latter regard, power on the island has been relatively stable of late, although Crawford does not expect this situation to last long. One area of concern has been the tendency for water to break through the Nafion drier, leading to measurement error. This situation is being remedied, however.

Problems because of the Nafion drier were major items in Fraser's report for Cape Grim, Tasmania. In this case, contrary to protocol, the drier had not been replaced for three years, with the result that recent measurements for the fluorocarbons appear to have been somewhat adversely affected. With the replacement of the drier on May 4, an immediate improvement in all species was observed. Fraser also reported that no data were obtained between July 1 and August 14, because of the lack of calibration gas. A calibration tank was mistakenly delivered to a private firm in Sydney, but it did eventually arrive at CSIRO. A zero-air generator was installed on July 12, and the sample loop volume for CH_4 was increased on July 29. Further details regarding the Tasmanian station are included in a report distributed at the meeting by Fraser.

On more general experimental matters, Crawford reported the welcome news that the new calibration tanks are performing well and are being stockpiled. With regard to obtaining enhanced CH_4 measurement precision from the HP 5880s, contacts with Hewlett-Packard engineers have not proven useful. Fraser indicated that he may pursue this matter further. Attempts to locate a source for more Porasil D have also not been successful, but Prinn agreed to continue to pursue this matter further and to inform Simmonds of any leads. Finally, it was generally agreed that the UPS's have been a major nuisance and expense, and any improvements in this technology (if it can be labelled such) would be very welcome.

Times and locations for the next two GAGE meetings were agreed to. The Seventh meeting will be held at the Cashel House Hotel near Galway, Ireland on May 9-11, 1988, with participants arriving on Sunday, May 8 and departing on Thursday, May 12. Simmonds will be the host. The Eighth Meeting will be held on November 12-13, 1987 at the Healesville Country Club, Melbourne, Australia with Fraser as host (the IGACP meeting is Nov. 7-11 and the SABOAC II meeting is Nov. 14-18 so people will be able to attend these Australian meetings also).

The first session of the meeting adjourned at 1:00 pm.

II. The meeting resumed at 2:15 pm, with Rasmussen joining the group shortly thereafter. A lengthy and frank discussion of OGC's future role in GAGE ensued, precipitated by a number of indications that Rasmussen's interest in, and commitment to the program appears to have waned in recent years. For example, the N_2O paper which was the responsibility of OGC still had not been produced, and Rasmussen recently attempted inexplicably to withdraw his name from the CH_3CCl_3 paper without contacting any of the authors. The GAGE team members each expressed their distress about this behavior to Rasmussen, who then apologized for his behavior. The group agreed to turn responsibility for the N_2O paper over to Prinn and Cunnold. Rasmussen indicated his desire to continue in GAGE, feeling that his personal contribution could best be in the direction of improving or developing new measurement techniques for gases of present and future interest to GAGE.

Discussion next turned to the data. A major milestone was celebrated when Alyea distributed computer disks containing finalized values of all the HP 5840 data recorded at the ALE station network. The ALE measurements program can now be said to have been completed! As for GAGE, a review of the data collected through June 1987 yielded the following action items.

Macehead, Ireland [NB: This marks the debut of data from this new station]

1. January-June 1987: Values associated with calibration tank 121, to be adjusted to remove obvious step jump (See also point 5 below).

Ragged Point, Barbados

2. December 1986-late February 1987: CH_4 values to be dropped because of water contamination problem. Simmonds to provide December date that marks the start of this problem.
3. January-February 1987: Simmonds to check CH_3CCl_3 , CCl_4 and some $F - 11$ data that appear also to be affected by water contamination problem.
4. June 1987: Simmonds to check on denticulate behavior of CCl_4 and odd behavior of other species.

Cape Meares, Oregon

5. July-December 1986: $F - 11 S$ and $F - 11 P$ drifted apart dramatically. Rasmussen and Crawford to check for possibility of co-eluting species in some of the old calibration tanks. [NB: The difference between $F - 11 S$ and $F - 11 P$ is apparent in a number of other cases]

at other stations as well. Although these have not all been singled out as individual action items, the result of this Oregon case will be applicable to them. Alyea will provide statistics of the occurrence of this behavior].

6. December 1986–July 1987: Monotonic nature of step jumps in CCl_4 associated with calibration tank changes to be investigated. Rasmussen and Crawford to check heritage of secondary and primary standards. [NB: This problem has also been observed for some other stations].
7. Early December 1986: Alyea to label data during this period as pollution.

Point Matatula, Samoa

8. June–December 1986: $F - 11 S$ and $F - 11 P$ differ greatly during regime of calibration tank 025. (See point 5 above).
9. January–early March 1987: $F - 12$ erratic behavior (because of wet Nafion drier) to be eliminated.
10. Early February–mid March 1987: $F - 113$ and CH_3CCl_3 erratic behavior (because of wet Nafion drier) to be eliminated.

Cape Grim Tasmania

11. 1985: Incidents of $F - 113$ erratic behavior to be rechecked by Fraser.
12. October–December 1986: $F - 113$ hand jobs to be assessed by Fraser.
13. July–December 1986: Alyea to process N_2O values done by hand and provided by Fraser.
14. January–May 1987: $F - 113$ to be measured by hand, depending on results obtained for point 12 above.
15. Middle February–early May 1987: Eliminate automatically integrated $F - 11$, $F - 12$ and $F - 113$ data, because of Nafion drier problem.
16. January–June 1987: N_2O to be redone by hand, depending upon success of results obtained for point 13 above.

The first day of the meeting adjourned at 7:30 pm.

III. The second day of the meeting began on Wednesday, November 18 at 9:10 am with Prinn, Alyea, Crawford, Cunnold, Fraser, Simmonds, and Rasmussen attending. Someone resembling Rosen was seen on the golf course but this could not surely have been him.

Alyea had already distributed 3 discs containing the complete and final *ALE* (HP 5840) data set to the group. A separate tape/disc compilation will be available for *GAGE* data. It was agreed that while the co-addition of *ALE* and *GAGE* data used in the recent *Science* and *J. Atmos. Chem.* papers is the desirable merging strategy for *ALE/GAGE* papers we would not produce such a merged data set for outside users.

Khalil did not attend to discuss whatever progress he may have made on the *ALE/GAGE* N_2O paper and this (together with his absence the previous day) was taken as a formal resignation on his part from the *ALE/GAGE* group. Pursuant to the previous days discussion, Prinn and Cunnold will take over the writing of the N_2O paper and will present a draft at the next meeting. This also means that Khalil will not be able to utilize any *ALE/GAGE* data in any independent N_2O paper he may wish to write.

For the HP 5840/5880 overlap paper, Cunnold presented a proposed outline. Discussion led to the conclusion that this paper should cover overlaps at all stations, address a variety of time scales depending on the station (Cape Grim obviously has the longest overlap), discuss the role of

calibration tank and carrier gas changes on variability, and address the advantages of high frequency for identifying and interpreting polluted air. A draft will be available at the next meeting.

Rasmussen then led a discussion on ways in which the calibration tank changes might better be made to provide additional information on the small jumps due to the changes. It was agreed that an intercomparison between the incoming and outgoing tank before the standard 4-monthly instrument-reconditioning procedures should become a part of the standard procedure for station visits.

Fraser discussed some aspects of the *GAGE F* - 113 data as a precursor to work on a paper. While *GAGE* fractional trends agree reasonably well with those of a Japanese group (Makide *et al.*) the Japanese absolute values are 30% larger than *GAGE* values. Prinn mentioned that Ray Weiss and he may be proposing shortly to do an independent calibration of several atmospheric halocarbons which may shed light on the discrepancy. Fraser next discussed emissions and noted that the recent Montreal international fluorocarbon agreements should ensure that *F* - 113 industrial production will be available; he will send some preliminary numbers to Cunnold and Prinn for 2D and 3D model runs which will provide information on lifetimes and absolute calibration.

For the NASA 1987 Ozone report, it was agreed that we would make available graphs through June 1986 of: *F* - 11 *P* (not *F* - 11 *S*), *F* - 12, CH_3CCl_3 , CCl_4 , and N_2O . Alyea will send photos to Fraser and all other *GAGE* folk. The graphs should be labelled preliminary data and acknowledge all *GAGE* folk by name in the captions (as in the 1985 NASA report).

All 4th year *GAGE* funding from NASA is apparently approved. NOAA is supporting Barbados for 3 years beginning Sept. 1987 but definite CMA support for this station is for 1 year beginning Nov. 1987. DOE (UK) funding for Macehead is for 2 years beginning Nov. 1987.

On possible new *GAGE* sites, Crawford reported that an old *ALE* HP 5840 has been recently sent to the USSR and he will go to Lithuania to attempt to set it up very soon (there are hints that "*Ivan*" may have already damaged the instrument). Prinn reported an enquiry to him from Wolfgang Seiler about setting up a *GAGE* station at Cape Point, S. Africa. There was discussion of the effects of proximity to Capetown (15 miles) and to a bird rookery. No firm conclusions were reached on this subject.

On the subject of possible *GAGE CO* measurements Rasmussen reported that he was sending a proposal to NSF to do *CO* real-time at Oregon and Samoa using the Trace Analytical detector. Fraser noted that there is already a Trace Analytical instrument at Cape Grim. Prinn noted that it would be sensible to wait until these real-time instruments are proven reliable in the field before proposing expansion to Barbados and Macehead. Alternative (spectroscopic) *CO* techniques need to be looked at also.

The interface between *GAGE* and AEROCE at Macehead and Ragged Point was discussed next. Prinn noted he had sent a letter to Joe Prospero concerning possible sources of contamination for *GAGE* and that he felt that the AEROCE people would be very responsible and responsive to the contamination and other potential problems. The proposal by Oltmans (NOAA) to add a Dasibi ozone instrument to the *GAGE* hut in Barbados led to a discussion led by Simmonds of whether the present building was adequate for this. In particular: is the air conditioning adequate?, will there be problems with the power supply?, will there be inadvertent disturbances by one operator of the other operator's instrument?, and finally, how much longer will the present building (which is rotting) last? It was decided to propose to NOAA that if the present *GAGE* building can be replaced by a somewhat larger and suitably partitioned (*GAGE/Oltmans*) building with the requisite air conditioning, power, and space requirements then cooperation with Oltmans would be entirely agreeable to the *GAGE* scientists.

The formal meeting was adjourned at 12:55 pm and informal subgroup discussions on a variety of topics filled the remainder of the day.

Minutes of the Seventh Meeting of *GAGE* Scientists
Ballynahinch Castle, Co. Galway, Ireland
May 9-11, 1988

I. The meeting began on Monday, May 9 at 9:15 am with the following *GAGE* scientists in attendance: Prinn, Alyea, Cunnold, Simmonds, Fraser and Rosen.

The minutes of the previous (sixth) meeting were approved, but for one minor change, after considering them in light of Rasmussen's written comments. By unanimous vote, the group reiterated its view expressed in the minutes of the sixth meeting that Dr. Khalil is not to be considered a member of the *GAGE* team and, therefore, not privileged to access unpublished *GAGE* data.

Alyea reported that he has not formally prepared any tapes containing *GAGE* HP 5880 data, because these data have yet to be completely finalized. The lack of tapes has posed a problem for group members trying to analyze the species time series, but the group was sympathetic to the demands on Alyea's time that creating preliminary tapes would involve. On a related matter, Alyea noted that budgetary constraints have posed a large burden in dealing with the vast amounts of *GAGE* data. In light of this situation, it was agreed to reduce the data processing task by not attempting to fill in measurements by hand when the chromatography fails, except when one week or more of automatic observations are missing.

Simmonds presented the results of a comparison of daily measurements made at Adrigole and Mace Head during September-December 1987. Overall, the agreement was excellent, thereby offering important support for the decision to reestablish an Irish station. The group offered its congratulations to Simmonds for successfully completing the hard work involved in this task. Fraser distributed plots of monthly means of the two stations since 1978, which demonstrated that the new Mace Head measurements are consistent with the trend observed in the old Adrigole *ALE* data.

The rest of the first session was devoted to an in-depth discussion of the manuscript drafted by Prinn about the N_2O *ALE/GAGE* data. The need to undertake a number of further calculations was highlighted, and remaining tasks were assigned to co-authors. Prinn asked everyone to respond with comments about the manuscript and to sign the agreement to be a co-author by 1 July.

Crawford joined the meeting at 12:45 pm, and the first session adjourned at 1:45 pm.

II. The meeting resumed at 2:40 pm with further discussion of the N_2O paper. After completing this item, Crawford distributed a note from Rasmussen expressing his regrets for not attending the meeting because of illness. The note also indicated Rasmussen's plans for the upcoming year

in light of budget cuts imposed, and directives issued, by NASA. Rasmussen's note also stated his intent to produce a manuscript on the stability of the calibration tanks before the end of the year, following his letter of 16 December to the group. The group expressed its pleasure at this plan, as well as its keen interest in seeing the time series plots for CCl_4 and N_2O calibrations as soon as possible.

Continuing with the topic of manuscripts in preparation, Fraser reported that because of other commitments he had not made progress on the paper comparing HP 5880 and HP 5840 data. He hoped to have a rough draft of this paper ready for the next *GAGE* meeting, however. Plans for a paper on the *GAGE* measurements of $F - 113$ were also discussed by Fraser. Our preliminary data for this species indicate a trend that is consistent with other estimates. Outstanding issues include the absolute calibration value for $F - 113$, for which there is currently large disagreement. Intercalibrations with Makide, and possibly others, is planned for later this year. Also, more information about emissions of $F - 113$, beyond the global numbers contained in the UNEP report, will be gathered by Simmonds and others. It was agreed, however, that the $F - 113$ manuscript should be given lower priority than the HP 5880 vs. HP 5840 paper.

The discussion turned next to funding matters. Prinn urged NASA grantees to submit their renewal proposals by June and to be aware of the possibility that the proposals may be subjected to peer review. Rosen reminded the group that his NASA contract will expire in June, which will mark the end of his formal involvement with the *ALE/GAGE* project. He did indicate his plans to submit an independent proposal to NASA this summer to do research with the *GAGE* data, and to include funds in the proposal budget to attend future *GAGE* meetings as a non-team member. Simmonds reported that the CMA will stop providing support for the Barbados station by October, and it is urgent, therefore, to find alternative support. Simmonds will notify NOAA of this development, and an attempt will be made to see if NOAA can make up the remainder of the monies now needed. The possibility of support from NASA, or even NSF, will also be explored. On positive notes, Simmonds and Fraser reported that funding for Mace Head and for Cape Grim seems secure for the next couple of years, although Fraser indicated that he needs to continue to obtain some additional industry support for his efforts.

Crawford next reported on his visit to Estonia, USSR, and his installation of an HP 5840 there. Although the instrument was set up in November, measurements from this site have yet to materialize, perhaps because of severe power problems at the station. The group agreed that when such data became routinely available to the *GAGE* team, it would be appropriate to invite

the Soviet scientists to a *GAGE* meeting.

The last item attended to at this session was to agree upon the venues for the next two *GAGE* meetings. The upcoming meeting will be held at the Peninsula Country Golf Club south of Melbourne, Australia on November 11-13. Attendees should plan to arrive on Thursday, November 10 and to depart on Monday, November 14. The following meeting will be held in the Boston area in May 1989.

The first day of the meeting then concluded at 6:00 pm.

III. Business resumed at 9 am on Tuesday with a review of the data from the stations for 1987. In light of the large amount of data now being considered in *GAGE*, a new protocol for recording action items on data problems was agreed to for all data taken beyond June 1987. This protocol requires each experimentalist to note the action items on the plots of his station's data record and to provide a copy of this material to Alyea.

Upon examining the January-June 1987 data for the second time, the following action items remain for each of the stations:

Mace Head, Ireland

1. Jan 1987: All measurements to be marked as pollution events.
2. late June 1987: Simmonds to correlate low CH_3CCl_3 values with on-site O_3 values.
3. mid-June 1987: Simmonds to check high CH_3CCl_3 values
4. Tank 121 values for CCl_4 to be adjusted.

Ragged Point, Barbados

5. June 1987: Denticulate behavior of $F - 11$, $F - 12$ and other species to be re-examined, along with the dip in N_2O .
6. January 1987: Eliminate the rest of the CCl_4 and CH_3CCl_3 data, because of the Nafion drier problem.
7. January 1987: CH_4 values to be reassessed, provided Rasmussen can provide contemporary flask values.

Point Matatula, Samoa

8. mid-January 1987: Eliminate $F - 113$ and CH_3CCl_3 , because of Nafion drier problem.

Discussion of the action items from the previous meeting related to the $F - 11S$ and $F - 11P$ differences and to the CCl_4 step jumps was delayed until the next day.

The meeting adjourned at 1:00 pm to allow the group to visit the Mace Head Station. Thomas O'Connor, who had joined the meeting in progress at 11:00 am, graciously hosted the group at the site. The group greatly enjoyed its visit and enthusiastically supported the selection of this facility as a *GAGE* station.

IV. The meeting resumed at 9:00 am on Wednesday morning with Crawford describing the history of the calibration tanks in order to provide background information for the discussions to follow. Given the complexity in the lineage of the tanks, it became clear that a certain amount of subjectivity was involved in assigning values to them. Crawford then made a lengthy presentation of his investigation into the source of the recent disagreement between $F - 11S$ and $F - 11P$ at some stations. Based on an extensive series of experiments at Cape Meares, Crawford was able to trace the problem at these stations to the presence of a large difference between the species concentration in the calibration tanks and ambient air, combined with a nonlinearity in the HP 5880 instrument $F - 11$ response. It was agreed, therefore, that in the future every attempt should be made to ensure that calibration tanks used at stations always contain "about" the same amount of each species as the air being measured at the stations. The precise criterion will be determined as the result of a field experiment that was also agreed upon. In this experiment, Crawford will create four flasks at OGC with a range of species concentrations (e.g., ambient, to ambient minus 60 pptv, for $F - 11$), and these will be shipped to the stations to be measured against the calibration tanks there. An outcome of this experiment will be to determine a correction factor to be applied to fix the $F - 11S/F - 11P$ offset problem where it occurred.

As for the CCl_4 problem, Simmonds suggested that it may be due to other sources, such as absorption in the calibration tanks. The above "four-flask" field experiment will include CCl_4 and further consideration of this problem will be needed if this field experiment is inconclusive with regard to CCl_4 .

At this point, discussion returned to the action items for the last station to be considered,

Gape Grim, Tasmania

9. mid February - early May 1987: Eliminate $F - 11$, $F - 12$ and $F - 113$ because of Nafion drier problem
10. mid May 1987: Check to see if spread in $F - 113$ values can be reduced by hand integration
11. October-December 1986: Drop $F - 113$ values.

It was also noted by the group that the measurements of $F - 113$ and N_2O at Tasmania are

still suffering from poor precision. Fraser agreed to send chromatograms showing the problem to Crawford, and Simmonds will send Fraser a different column to try to improve the N_2O situation.

The session adjourned at 1:15 pm.

V. The final session, which began at 10:15 pm on Wednesday night, was devoted to reports on the present status of the stations. At Cape Grim, Fraser reported, there have been a large number of power outages, with the event of 3 March causing the instrument to be locked into a mode that prevents it from automatically transferring its data to the computer. Although it has been possible to save these data by manually recording them, this labor-intensive process cannot continue much longer, and efforts are being made to fix the problem. Because of a problem with venting of gas from the calibration tank, it was necessary to turn off the machine on 12 April until a replacement tank is installed sometime during May. Fraser provided his usual comprehensive written report on Cape Grim in addition to the above oral comments.

Crawford reported that the instrument in Samoa is currently running but not optimally. He visited the site in March, but since then a board became defective. It will be replaced during his next site visit in June. The UPS at Samoa is only marginally healthy, and ambient air measurements are beginning to show occasional signs of erratic behavior. Crawford also reported that the Cape Meares station has been running well lately, with no break-ins.

At Mace Head, Simmonds reported that, for some unknown reason, the precision of the $F - 12$ (and N_2O) measurements has deteriorated, although hand measurements of the chromatograms may improve this situation. An overhaul of the system is planned to remove possible contaminants from it. The station at Barbados required an emergency visit, because of a variety of problems with regulators, boards, etc. In particular, the CH_4 data became quite noisy, because the FID was generating electronic interference. Simmonds replaced the FID, and although this solution appeared to work, we are currently not getting any CH_4 data there, for an unknown reason.

The seventh meeting of *GAGE* scientists then formally concluded at 11:55 pm.

Minutes of the Eight Meeting of GAGE Scientists
Peninsula Country Golf Club, Frankston, Victoria, Australia
November 11-13, 1988

- (1) The meeting began on Friday, November 11, at 9:00 am with the following GAGE scientists in attendance: Drs. Prinn, Crawford, Alyea, Fraser, and Simmonds.

The minutes of the previous (seventh) meeting were approved as written. The agenda for the eight meeting was rearranged somewhat from the one distributed to allow Dr. Prather (NASA) to be present when the latest GAGE data was reviewed.

Crawford described the currently available results of the "four-flask" experiment which was designed to quantify any non-linearity in instrumental response at each of the GAGE sites. For F11 the Cape Meares and Samoa instruments showed non-linearity below about 240 pptv while the instrument at Mace Head and the Perkin-Elmer at OGC were essentially linear throughout. For F12, F13, and CH_3CCl_3 on these instruments there is no evidence for non-linearity. Some non-linearity is apparent for N_2O but the difference between air and calibration concentrations is generally too small to make this a consideration. For CCl_4 the small flasks appeared to produce instability so the experiment is not definitive for this species. The "four-flask" experiment has not yet been carried out at Cape Grim or Barbados but it will be done in the near future.

Based on the data available and subject to the results from the remaining two instruments yet to be evaluated, general correction formulas were devised to slightly adjust *a posteriori* the assigned calibration tank values for those tanks where the difference between air and calibration concentrations was sufficient to make non-linearity a consideration.

Next the group moved to a general discussion of the status of calibration in GAGE. Due to the general exhaustion of the old "primary" standard tanks (e.g. BY1, 003, etc.) "daughter primary" tanks have been used in the last couple of years to calibrate the "secondary" tanks sent to the sites. It was agreed that it was time for an in-depth check of the accuracy of this new procedure by a "direct comparison experiment" in which selected secondary tanks would be compared directly to a remaining healthy primary tank (specifically 002). Preliminary work by Crawford along these lines has indicated that corrections to the CCl_4 values assigned to certain secondary tanks are required and he will now proceed to assess whether corrections are also required for the other GAGE species.

Due to the fact that the N_2O 9-year paper has considerable urgency Crawford agreed to first address N_2O in the above direct comparison experiment. Also the general importance of the calibration issue together with the fact that NASA has asked *GAGE* to submit a full new proposal next June led the group to agree to meet two months earlier than the usual May time frame with the exact time and place (Boston or Oregon) to be decided between Prinn and Crawford. The meeting after that will be in the usual October/November time frame and will be in Georgia with Alyea as host.

Further on the calibration issue, it was agreed that each Station Scientist should possess enough of his own tanks at (or available for) each site so that temporary "*tertiary standards*" can be made from the on-site secondary standard in the event that new secondary standards do not arrive from OGC on time. This would eliminate the possibility of significant data gaps due to late arriving tanks or other eventualities.

Discussion then moved to interactions between *GAGE* and other groups. Crawford gave an update on the Soviet operation of the old *ALE* HP 5840 in Estonia. Communication between Koropolev and Crawford continues, Koropolev has done some flask sampling, but there is still no real-time data. The group reiterated its statement made at the previous meeting that Koropolev would be invited to attend a *GAGE* meeting only after he has real-time data to contribute.

Aeroce has moved into both Mace Head and Ragged Point. Simmonds will explore the possibility of moving the *GAGE* air intakes to the top of the Aeroce towers at each site. At Ragged Point the Aeroce tower is up and the building is up. Oltmans has not installed an ozone instrument yet at this site. At Mace Head the new road is in and the new tower and van will shortly be in. Irish funding for a small building is available (about 20' x 14'). At the next meeting we should discuss whether *GAGE* should move into this new Irish building. Continued vigilance and caution will be necessary to see that Aeroce operations do not contaminate *GAGE* measurements.

Concerning Samoa, Prinn has approached NOAA (Albritton, Elkins) to ask when GMCC will be ready to do a double-blind intercomparison of their real-time Samoan data with *GAGE* Samoan data. No official reply has been received but it is apparent that there are continuing problems with GMCC's real-time network which have not yet been resolved. This conclusion was corroborated by Crawford's very limited observations of GMCC operations at Samoa. The *GAGE* team has been ready to compare for the past year so the delays in timing of this crucial comparison are totally in GMCC hands.

The group recessed at 3:00 pm and reconvened at 7:00 pm. Prinn distributed copies of

his second draft of the *ALE/GAGE N₂O* paper. He emphasized that the major conclusion from the first draft-namely that fossil fuel combustion alone cannot explain the gradients and trends in *N₂O* - still stands. The paper is in near final form but some more "fine-tuning" model runs are needed and the issue of the validity of calibration for the last 2 years of the 9-year *N₂O* record needs to be checked as discussed earlier. If necessary a paper addressing only the first 7 years will be submitted. Work continues on the instrument intercomparison paper but no manuscript is in sight. Fraser and Prinn discussed some preliminary work they had done toward an *F113* paper : namely a calibration intercomparison (Makide, Cicerone, Penkett, *GAGE*) to be carried out by Fraser, and 3D model *F113* lifetimes and emissions computed by Prinn and Golombek. Currently it appears that the best estimate for the calibration factor for *F113* is around 1.4.

The Friday meeting adjourned at 8:00 pm.

- (2) The second day of the meeting began at 8:30 am and the group was joined by Dr. Prather representing our NASA sponsor.

Work began immediately on a review of the data at each station beginning with the latest 6 months (January-June 1988) and working back first to discussion of action items for the July-December 1987 data and then earlier data.

A. The action items for Barbados are:

1. Mid-to-end of June 1988 - check all species
2. April 1988 - first week of data. No calibrations?
3. June 24, 1988 - reason for *F113* negative dip?
4. November 1986 - February 1987. Are the low methane values perhaps due to water problems? Test FID sensitivity with water saturated system to determine possible water correction factor?

B. The action items for Mace Head are:

1. Dip in all species from March 1-15, 1988 to be investigated.
2. Look at methane in second week of June 1988.
3. Look at very high methane value on March 28, 1988.
4. Also look at large slope in methane data beginning March 24, 1988.
5. Remove *N₂O* pollution in early October 1987, and end of October through early November 1987, and early December 1987. Also check whether July 20 was a pollution episode.

6. Insert correct values for tank 121 in the 1987 data.
7. Check *F113* from August 20-September 20, 1987. Also check December 1987 which has low *F113*.
8. June 1987. Check four or five very high CH_3CCl_3 values.

C. The action items for Samoa are:

1. Remove Nafion-related problem data up to February 25 in 1/88 to 6/88 data.
2. Remove Nafion-related problem data up to June 9 in 1/88 to 6/88 data.
3. Why does *F11* change for the worse on February 26 1988?
4. Check all *F11* high values in 1/88 to 6/88 period
5. Why no data 12/10/87 to 12/31/87?
6. Delete one point at end of September 1987 for *F12*
7. Make sure N_2O data is deleted along with other data in October 1987.
8. Hand measure *F113* in July 1987.

D. The action items for Cape Meares are:

1. Check tank change 341-350 in 1/88 to 6/88 period. Note *F12* drop.
2. Check tank 341 for possible drifts affecting 7/87 to 12/87 data.
3. Check bad methane in July 1987

E. The action items for Tasmania are:

1. For *F113* in all of 1987 try manual measurements again taking 4 points each day. In the future try temperature programming and make sure peak is attenuated to ensure good peak height for ruler measurement.
2. For N_2O check on March 10 1988 for possible pollution.
3. Jumps between tanks 343-351 to be checked.

As an extra data item Simmonds presented the results of the few month overlap of the *ALE* HP 5840 at Adrigole and the *GAGE* HP 5880 at Mace Head. The correlation was very high and assures us that the records at Adrigole and Mace Head can be considered closely comparable.

The meeting then proceeded to the station reports. At Mace Head Simmonds, reported that there has been relatively few problems with only the occasional power failure disrupting data collection. The problem with poor *F12* and N_2O chromatography resolved itself when the carrier gas cylinder was changed. The only real problem resulted from a delay caused by Customs in obtaining a calibration tank. No calibration data was consequently acquired from July 30 1988 until August 23 1988 when the new tank was installed. The Aeroce road was constructed beginning 1987 through 1988 and runs between

the present *GAGE* site and the *AEROCE* shoreline site. Aeroce plans to install their tower and laboratory at this shoreline site in the Spring of 1989.

All of the problems with the methane analysis at Barbados were resolved during the site visit in early June 1988. The methane analysis since then has been excellent. A new problem developed in mid-July 1988 when the valve on the silicone channel failed to inject samples. At first this was thought to be caused by a leaking air actuator. However, installation of a new air actuator did not fix the problem. During an emergency site visit in the first week of September the S-channel gas sampling valve was replaced restoring correct operation of the S-channel. As a result of this valve problem about 7 weeks of S-channel data was lost. Calibration gas ran out in October 1988 with about a 3 week delay in obtaining the replacement tank which was held by Customs due to lost paperwork. The station was repainted and a new door fitted during the September site visit.

At Cape Meares Crawford reported that problems are developing due to aging of the Porasil column. Simmonds noted that he will be attempting in the near future to obtain a new Porasil-D supply for *GAGE*. High baseline noise in methane at Cape Meares continues and it has proved difficult to isolate the problem – work is continuing. Power failures are increasing at this site making the acquisition of an expensive UPS possibly being required in the future.

At Samoa Crawford noted that the UPS is out and new boards and batteries have been ordered. All equipment is presently on Island power (which is very poor) and we will need to remain on it for 6-12 months. There is continuing praise from the Samoa site NOAA personnel concerning the small amount of labor involved with *GAGE* equipment compared to GMCC equipment. Nevertheless these personnel still find difficulties with replacement of the *GAGE* Nafion driers. Crawford has now installed a weather data gathering system at this *GAGE* site.

At Cape Grim Fraser reported that a problem with the HP 5880 - GRIMCO interface between March 3 and May 18 necessitated manual transfer of data to GRIMCO. Due to the lack of a calibration tank no data was taken between April 12 and May 27. A number of power failures occurred in the May-September time period. A Porasil D column provided by Simmonds was installed on July 21 but did not unfortunately improve the N_2O analysis as hoped – the old column was reinstalled on July 27. A new molecular sieve column was installed on July 26 giving some improvement to CH_4 analyses. Additional information is given in Fraser's written station report.

Several NASA-related issues were then discussed by Dr. Prather. First, the NASA

grants to MIT, Georgia Tech, and OGC have been approved for the November 1988 - October 1989 time period but there is still apparently some paperwork to be done at the OGC end to finalize the funding to OGC. NASA has agreed in principle to provide partial funding for one year to help support the *GAGE* Barbados station with the remainder to come from NOAA - details of the contract procedures still need to be worked out. Prather discussed the desirability of a NASA-sponsored meeting in the April 1989 time frame devoted to a discussion of future directions for *GAGE*. Both *GAGE* and non-*GAGE* scientists would be involved. As noted earlier, a full proposal from all *GAGE* investigators is needed in June. Prather also mentioned NASA plans for providing data from various NASA "*campaigns*" (e.g. STEP, Antarctic ozone expedition, etc.) to outside users in the form of compact discs. The *GAGE* scientists endorsed the idea of including all *GAGE* data on these discs for public dissemination.

Finally, the discourse at various points during the meeting concerning certain problems areas in *GAGE* (e.g. apparent lack of sufficient numbers of calibration tanks at OGC, the need for a new look at long-term calibration procedures at OGC, etc.) led to a frank discussion of ways of resolving these problems which will be considered in earnest over the next few months.

The second day of the meeting was adjourned at 6:00 pm.

- (3) On the third day (Sunday) Drs. Prinn, Fraser, Crawford, and Prather flew to Tasmania to inspect the Cape Grim *GAGE* facility.

**Minutes of the Ninth Meeting of GAGE Scientists
Massachusetts Institute of Technology
March 15-16, 1989**

DAY 1

The meeting began on Wednesday March 15 at 9:00 am with the following in attendance Alyea, Cunnold, Crawford, Fraser, Prinn, Rasmussen, Rosen and Simmonds. The minutes of the eight meeting were approved as written.

Crawford presented the 6-month station reports for Cape Meares and Samoa. Ageing of the Porasil-D is a continuing problem at Cape Meares. Some power failures have occurred and there have been strong winds (the winds speed cups have sometimes been dislodged). The past problems with break-ins have apparently ceased with the new disc locks. Baseline noise in CH₄ is still evident – the other species look OK. At Samoa the power is still unreliable but the NOAA generator provides backup. Our UPS is working. The data generally appears of good quality. A new director for the NOAA operations here is due soon (also a new ET). The station lease is to be renewed in May. Local political problems may accrue with a new village chief appointment.

Simmonds presented the semi-annual status reports for Barbados and Mace Head. At Barbados problems developed on January 16 on the Porasil channel where the sensitivity dropped by a factor of two. The problem was finally corrected by a site visit on March 10 with replacement of a valve rotor and a gas solenoid. The methane and silicone channel data appeared to be unaffected by this problem. The station roof was replaced in January. The new caretaker at Barbados (Peter Seeley) is very reliable and is doing very well. At Mace Head the instrument has performed very well and there have been no major problems since January (the last site visit). The AEROCE tower is expected to arrive in April or May. The new building nearer the shoreline is completed and Simmonds anticipated moving the GAGE operations into this building during either the May or September site visits. Mace Head was featured in a BBC program on the greenhouse effect in early January!!! Fraser presented the Tasmanian report. A severe lightning storm caused a power failure on November 21 – the station 22 Kv transformer was destroyed and replaced on December 7 and the station diesel generator was used in the intervening period. Otherwise, Cape Grim data are OK. Fraser reported that CSIRO has been offered space for a GC at Macquarie Island (55°S) and suggested that we discuss the possibility of a GAGE station at this site – discussion was postponed until the next meeting. Other details of the status of Cape Grim are available in Fraser's written station report.

Following the station reports, discussion moved to some important experimental topics. First the idea of overlapping calibration tanks was discussed. The new GAGE tanks (32ℓ, 600 psi, with new valve) ought to last for 6 months with 12 analyses per day or 12 months with 6 analyses per day. Thus using two tanks alternately and replacing them every 12 months (but 6-months out of phase) provides considerable protection against both lost data and large data "jumps" at tank changes, and will improve considerably the definition of the annual cycle (since it is measured against one tank). The group moved to adopt the procedure as soon as practicable. Rasmussen noted that 20 of the new GAGE tanks were now available at OGC with this total increasing to 25 shortly – hence there are enough GAGE tanks to implement the scheme.

Next, the group discussed the dwindling global Porasil-D supply. Simmonds said he has examined the patent and it may be possible to produce Porasil-D from A, B, or C by sintering with Na_2O . He will pursue this. He also proposes to advertise the need in the Journal of Chromatography (Rasmussen said he will do the same in some trade newsletters).

The discussion then turned to possible future instrument upgrades. Rasmussen and Crawford suggested using a dedicated Porapak Q/ECD channel for N_2O and moving CH_4 analyses to a separate instrument. Fraser expressed reservations about the latter. Simmonds suggested using a 9-foot Porasil column to improve N_2O analyses (CFC-12 would also be obtained but not CFC-11). Prinn noted that the next new compounds for GAGE to consider should be the hydrogenated species CFC-22 and CFC-123 as these have lesser environmental impacts (shorter lifetimes) than the current ones. Crawford and Simmonds led a discussion of methods for analysing these latter two species – Simmonds will get samples for trial analyses prior to submission of the new GAGE proposal.

Rasmussen unfortunately had to leave the meeting in the early afternoon of the first day.

During a brief discussion of funding matters Prinn noted that although it appeared that the 6th year of NASA funding (1989-1990) was in hand, a new and complete proposal to NASA for GAGE would be required in June 1990. The UK funding for Mace Head will be up for renewal soon. Fraser reported no important known problems with future Cape Grim support from Australia. Barbados will continue to receive joint NOAA/NASA support for the 6th year. Discussion then moved to publications with Prinn distributing his third draft of the N_2O paper. He noted that the conclusions are still preliminary pending the results of the tests of the OGC working standards to be discussed later in the meeting. Two other papers are being contemplated but no drafts are available. Discussion then began on the HP 5880 data through June 1988 and continued into the next day. The first day was adjourned at 5:45 pm.

DAY 2

The second day began at 9:00 am. The review of the data up to June 1988 produced the following action items ("old" action items referred to here are listed in the minutes of the Eighth GAGE meeting):

A. Barbados

1. (see old action item A4) - drop the last 5 or 6 days in November 1986 and through the next calibration tank change in February 1987.

B. Mace Head

1. (see old B3 and B4) - Peter will recheck these CH_4 items (second week in June 88, also March 28, 88) and advise.
2. (see second part of old B7) - check that the December 87 CFC-113 values have been replaced.

C. Samoa

1. (see old C3) - remove the approximately 5 days of data (humps) in late February - early March 88 occurring after major equipment changes.
2. calibration tank 355 to be checked.

D. Cape Meares

1. No action items.

E. Tasmania

1. (see old action items E1, E2, E3) - these still have to be completed.

Discussion of some major calibration issues began with Crawford presenting the results of the "8-flask" experiment for documenting the degree of non-linearity of all GAGE instruments. It is apparent from these non-linearities that we are at the point where the concentration differences between the primary OGC standards and the current atmosphere are large enough for some GAGE species to warrant concern. This is true particularly for CFC-11 analyses where non-linearity manifests itself as small but statistically significant differences between the S-channel and P-channel analyses. A formula for correcting the CFCl_3 data based on the non-linearity studies was approved by the group to be used in cases where the difference between the uncorrected S and P analyses exceeds 3 pptv.

Crawford also presented the results of the "direct comparison" experiment designed to test the validity of the suspect post-1985 working primary standards at OGC. Crawford has now recalibrated these working primary standards against the remaining original primary standard (specifically tank 033) at OGC and produced corrected values for all secondary tanks sent out to the sites. For some compounds (e.g., N_2O) the corrections are small but for CCl_4 in particular the corrections are very significant. The group thanked Crawford for the considerable extra effort he put in to resolve this problem.

Unfortunately, the data processing for all data from mid-1985 onwards will now need to be repeated. Fortunately, our suspicions about the OGC standards led us to hold back from releasing (or worse publishing) the post-1985 data until this problem was resolved. It was decided that N_2O reprocessing would get priority so the N_2O paper can proceed to submission to *JGR*.

A frank discussion then began about how to resolve a number of the on-going calibration and other problems in GAGE and how to include these resolutions in the new GAGE proposal. The possibility of bringing a new experimentalist to play a major role in calibration was addressed specifically. It was agreed that some major changes in the present structure are necessary to attain the science goals. Prinn agreed to begin the task of writing the new proposal and to explore the possibility of introducing new players in GAGE.

The ninth meeting of GAGE adjourned at 6:00 pm.

Minutes of the Tenth Meeting of GAGE Scientists
Stone Mountain, GA, November 2-3, 1989

November 2

The meeting began at 9:00 am with the following in attendance: Alyea, Crawford, Cunnold, Fraser, Prinn, and Weiss. The group welcomed Ray Weiss who was about to join the experiment in its new version (tentatively named Advanced Global Atmospheric Gases Experiment). A brief review of the minutes of the ninth meeting resulted in their approval without alteration.

The following reports on the present status of the GAGE stations were presented:

- (a) **Mace Head (Simmonds)** - Many problems (necessitating 15 site visits) occurred. Contaminated gas tanks delivered in April 1989 caused several blocks of data to be rejected. The AADCO air compressor failed in May 1989 and some methane data was lost. During an emergency visit in June 1989 both valve rotors were replaced and a problem was discovered with the valve actuators - this ultimately caused destruction of the valves themselves. On July 9, 1989 the GAGE equipment was moved to the new building near the shoreline and the GAGE air sampling line was relocated 30 ft up on the AEROCE tower. Another site visit in September 1989 to fix several mechanical problems revealed difficulties with the silicone channel ECD. Specifically, the detector sensitivity was deteriorating rapidly and a new ECD was ordered. This new detector was installed during the October 1989 site visit. No calibration tanks have been sent by OGC to this site since December 1988 and Simmonds expressed concern about this. Only one tank at 400 psi is on hand. The possibility of a salmon farm opening up off-shore at Mace Head was discussed. Simmonds and Prinn have both sent letters to Dr. O'Connor expressing concern about the effects of such a farm on GAGE.
- (b) **Barbados (Simmonds)** - no real problems in the last 6 months. Service visits were made in June and October 1989. Silicone valve rotors were replaced in October 1989. The ECD on the Porasil channel which had become noisy was replaced by a recently cleaned and repaired ECD. The building in Barbados is deteriorating and will soon need to be replaced.
- (c) **Cape Meares (Crawford)** - at the time of Crawford's departure from OGC in June the Porasil column was deteriorating. Jim Mohan with help from Don Sterns is apparently now carrying out Crawford's tasks at this station (fortunately the day-to-day caretaker Fred Thone is continuing). With Rasmussen not attending the meeting no further information was available.
- (d) **Point Matatula (Crawford)** - Jim Mohan had visited the station recently and had called Crawford several times while there. The data appeared good except for some temporary difficulties with methane which may be related to water in the system or to a programming problem. Unfortunately Emily Wilson has left the NOAA staff and her replacement has proven less than reliable. At the time of the meeting the UPS was not working and the GAGE machine was on Samoan power. Fred Alyea noted that he had received no data at his end from this station since June 1989. Rasmussen had told Alyea that he would Federal Express the station logs to him but they have not yet arrived.
- (e) **Cape Grim (Fraser)** - a number of power failures occurred largely in March and April 1989. Calibration tank R-363 was replaced by R-366 on June 27. Occasional flask sampling continued through this period in addition to the real-time measurements. The hydrogen cylinders were changed on June 14 and September 1, the nitrogen cylinder on June 16, and the Ar-CH₄ cylinders on March 30, May 30, and June 8. The nitrogen-line mole sieve was changed on April 11 and the Nafion dryer on April 12 and September 14. Injector valve no. 1 was sticking on

August 28, September 7, and September 12 - this was fixed by increasing the valve actuator pressure on September 12. The methane sample loop was changed from 5 to 3 ml on June 14. On June 20-22 an attempt to integrate the CH_4 peaks using the HP 3390 was unsuccessful. Fires were reported near the station on March 17 and June 6 and crop dusting on June 19. Fraser visited the station on May 18-19. The Porasil column was replaced on October 2, 1989 and Fraser showed some sample chromatograms and data which resulted. A new computer is being installed at Cape Grim which may enable permanent storage of actual chromatograms on optical discs.

Attention then shifted to the HP 5880 data through June 88. Alyea will check on the 6 action items listed in the GAGE 9 minutes and notify the team if any of these items have not been done or cannot be done.

Next, the first review of data for July 1988 through June 1989 was undertaken. The following action items resulted:

(a) Ireland

- I1. Fraser to do back trajectory for mid-October 1988 pollution event.
- I2. Key "x" the January 1987 - September 1988 F113 data to warn the reader about the adjustments made by Simmonds to account for the effects of a contaminated regulator (due to Viton in regulator). The adjustment factor is about 1.12 -- Simmonds will confirm this and provide an estimate of the uncertainty on this factor and a description of the details of the adjustments to the GAGE team.
- I3. Check March 10 - April 10 period where noisy data is evident for all species except F11 on the S column.
- I4. Check January - March CH_3CCl_3 low values
- I5. Check CCl_4 values for the tank 350 to tank 368 transition.
- I6. Check March 28 - May 15 period in which anomalously high and low CH_4 values appear.

(b) Barbados

- B1. For mid-June to the end of July discard all S-column data due to failing actuator/injector.
- B2. Drop October data prior to the October tank change for all species -- the reason is the exhaustion of the calibration gas.
- B3. Drop all August 11-16 P-column data -- the reason is a failing solenoid.
- B4. For January 13 - March 10, drop all P-column data due to water in the Nafion drier.
- B5. For January 25 - March 10, drop all CH_4 data due to water contamination.

(c) Oregon

- O1. Apply missing F11S and F11P nonlinearity corrections to tanks 344 data.
- O2. Check F113 and CH_3CCl_3 values in tanks 350, 358, and 344 -- these tanks span a "dip" in the measurements for these species.
- O3. Check also the CCl_4 values in tanks 344 and 355.

(d) **Samoa**

- S1. For March 23 to April 15, delete data for all species due to faulty Nafion drier.
- S2. Check CH₄ values for tanks 359 and 349.

(e) **Tasmania**

- T1. F11S and F11P nonlinearity corrections yet to be applied to data calibrated against tank 363.
- T2. Fraser to examine F113 chromatograms for May through July to explain "quantization" effect.

Next the group discussed methodologies and rationale for hydrochlorofluorocarbon (HCFC) analyses. Simmonds gave an update of his initial experiments (which were summarized in the AGAGE proposal) for using the GC/ECD method for HCFC-22 (CHClF₂) and HCFC-123 (CHCl₂CF₃). He also described his apparently successful attempts to convert Porasil C to "pseudo-Porasil D". On pseudo-Porasil D (but not on Porasil C) he obtained good separation of HCFC-22 from CFC-12. For HCFC-123 there is still the problem of the proximity of the HCFC-123 and CFC-11 peaks.

The Group then reviewed the presentation which it had agreed to give to NASA Headquarters personnel the following day. Depending on the degree of involvement of Dr. Rasmussen in AGAGE, two acceptable courses of action were agreed upon to present to NASA: one with Dr. Rasmussen playing a role and the other with him not being involved. The meeting adjourned at 6:00 pm.

November 3

The second day of the meeting began at 9:00 am with the news that Dr. Prather but not Drs. Kurylo and Watson would be joining the meeting from NASA.

While awaiting the arrival of Dr. Prather, the group moved to discuss new calibration procedures. It is apparent that the new high pressure "Spectrasil" tanks could last for up to two years at the stations but some concern was expressed about recognition of drifts of species concentrations in these tanks. With two of these tanks overlapping and intercomparisons of incoming and outgoing tanks, it was agreed that this concern could be alleviated. Problems about obtaining and distributing the new tanks in a timely way were discussed. The need for a common "manual of operations" for all caretakers at the GAGE sites was expressed and received sympathy. It was noted that there are three ways in which the new calibrations to be developed by Weiss can be linked to the present GAGE calibrations: first through the remaining stored secondaries at the sites (particularly Tasmania), second through the Cape Grim "air-bank" contained in GAGE-type tanks filled annually and available back to 1978, and third through access to tank 033 at OGC if that is feasible.

With the arrival of Dr. Prather a frank and lengthy discussion began led by Drs. Prinn and Weiss on the topics of the AGAGE budget, the inclusion of HCFCs in AGAGE, and

the two scenarios developed the previous day for linking the present GAGE with the future AGAGE. Dr. Prather then returned to NASA Headquarters.

The meeting continued with a discussion of ongoing data interpretation and preparation of papers for publication. Prinn noted that the N_2O paper has been submitted to *JGR* and we are awaiting reviews. Fraser distributed a draft of the paper "Lifetime and emission estimates of 1, 1,2-trichlorotrifluoroethane (CFC-113) from daily global background observations: 1984-1989" for discussion and comments. Prinn noted that his and Golombek's global 3D model study of CFC-113 has just appeared in *Geophysical Research Letters* (vol. 16, p. 1153, 1989). Cunnold gave his opinions on the quality of the 11-year data record for several GAGE species noting some lingering discrepancies that may or may not be addressed by Weiss' new calibrations.

On the issue of future meetings it was agreed that the next meeting will be in early May 1990 at the Scripps Institution of Oceanography and be hosted by Dr. Weiss. The following meeting will be in Barbados in November 1990 to be hosted by Dr. Simmonds and to precede or follow his Barbados site visit. A tentative meeting was set for April 1991 in Tasmania with Dr. Fraser as host.

During the afternoon a telephone link was made with NASA Headquarters to enable several of the GAGE scientists to talk to Drs. Watson and Kurylo (and with Dr. Prather who had by then returned) on a number of important issues.

The tenth meeting of GAGE was completed officially at 5:30 pm.

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- 31 Dec. 1989 (Georgia Inst. of
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METHANE/ NITROGEN OXIDES/ POLLUTION MONITORING

ABST: The GAGE program is a team effort involving several institutions in the
United States, Great Britain, and Australia to measure and analyze, at
five global sites, a number of long-lived atmospheric trace gases of
importance to man and the environment. The gases involved are both
biogenic and anthropogenic in origin and include the trace species CFC13,
CFC12, CFC113, CFC14, N2O, CH4, and CFC11CFC12. Measurements are made at
each site several times daily using automated gas chromatographs. Since
the GAGE program is a cooperative effort involving scientists from several
organizations around the world, the details of GAGE progress during the

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